Inhibition of Vapor Cloud Explosions

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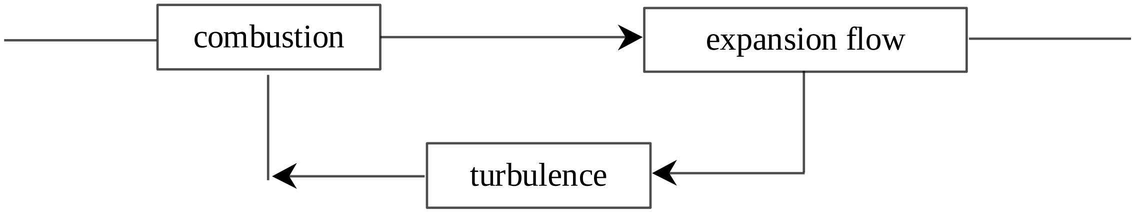
31st Annual European AIChE Seminar

23 April

The Hague

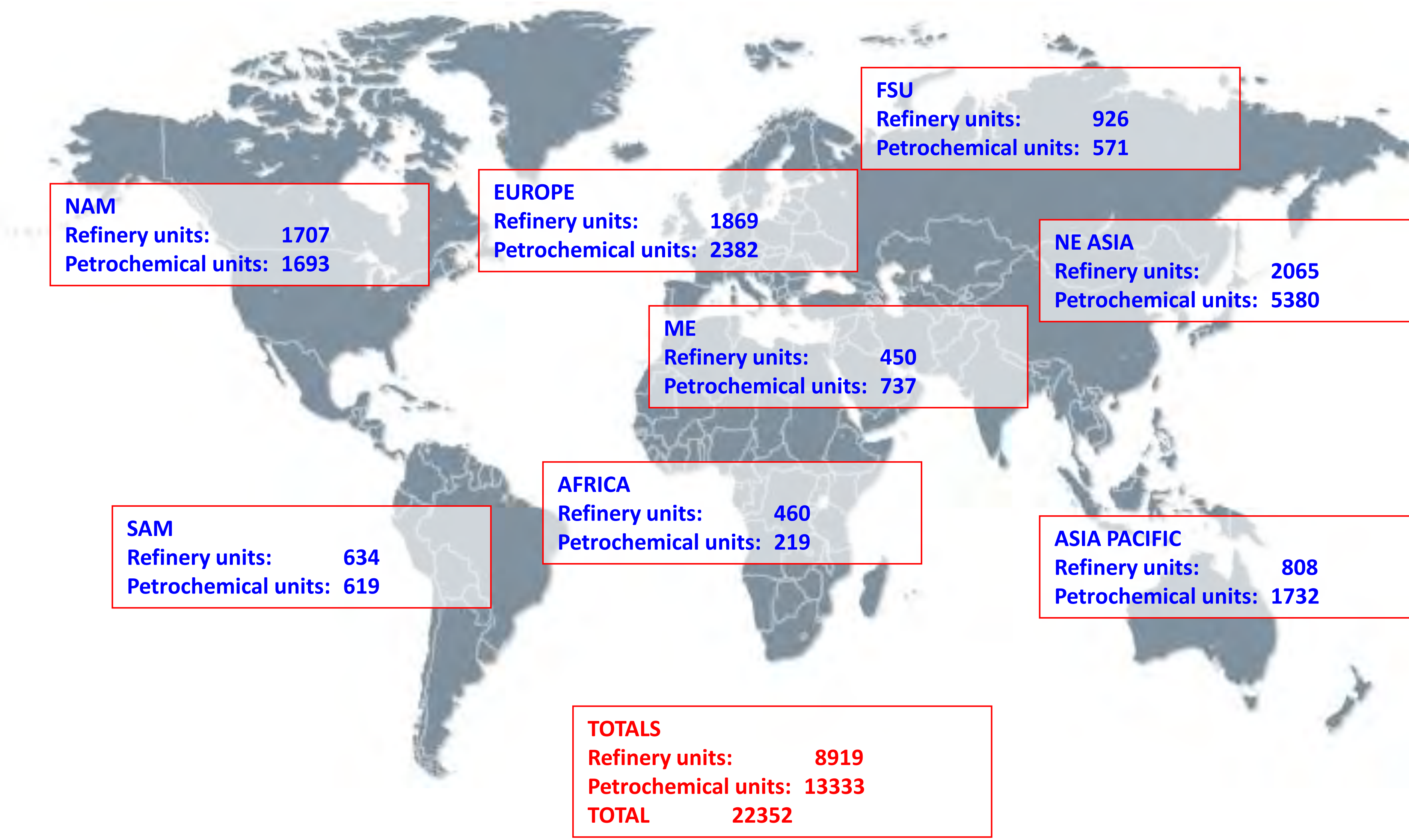
Vapor Cloud Explosions


combustion
expansion flow
turbulence

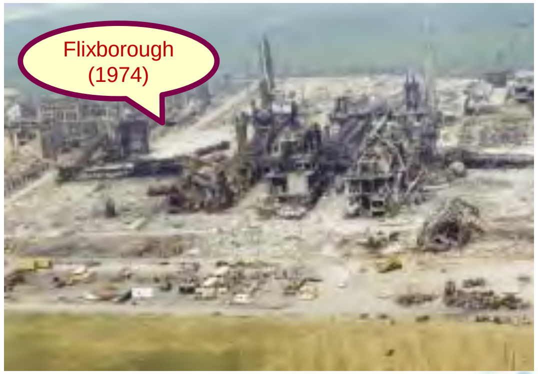
Detonations

Industrial examples of congestion

Refinery units and petrochemical units in the world



Impact on society can be dramatic…




Limestone in coal mine

Experimental Study on Inhibitors

Experimental program 2008-2010

- Purpose:
  - ✓ To determine the relationship between inhibitor characteristics (concentration, type, etc.) and flame combustion velocity of a fuel-air mixture (20 l vessel)
  - ✓ To verify the effectiveness of inhibitors in medium scale conditions (50 m^3)

- Number of tests:
  - ✓ 316 experiments in a 20 l vessel
  - ✓ 103 experiments in a 50 m^3 modules

Experimental program 2008-2010

Inhibitors tested

- Sodium chloride
- Sodium bicarbonate
- Calcium sulphate
- Manganese (II) carbonate
- Magnesium carbonate
- Potassium bicarbonate
- Potassium carbonate

Compounds tested

- Methane
- Ethane
- Propane
- N-butane
- Ethylene
- Propylene
- 1-butene
- Acetylene
- Hydrogen

- Potassium bicarbonate
- Sodium bicarbonate;
- Sodium chloride;
- Irganox and Irgafos
- Potassium carbonate

- Methane
- Ethane
- Propane
- Propylene
- Butane
- Butene

Experimental program 2008-2010 : measurements

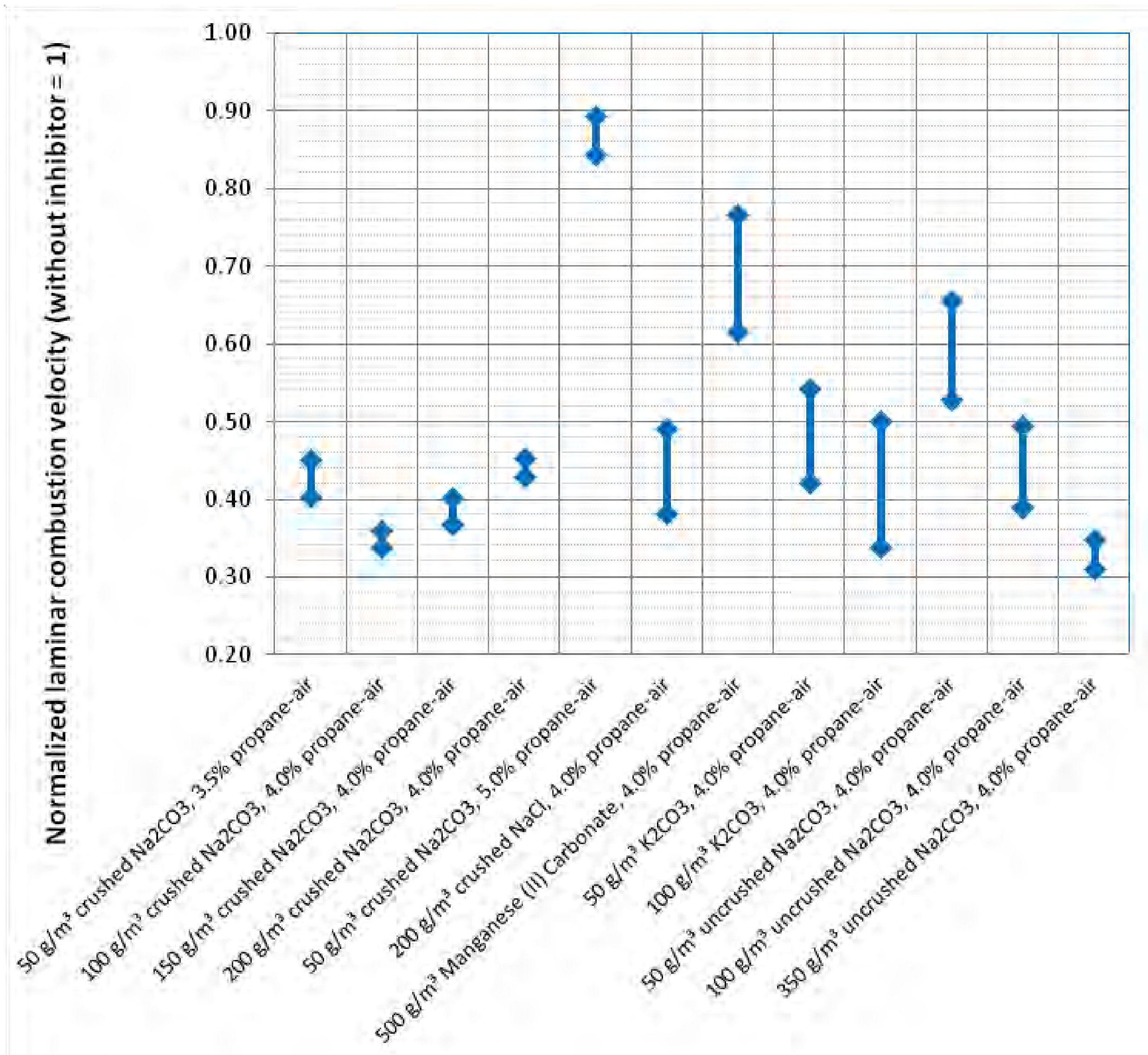
316 tests in a 20 l vessel

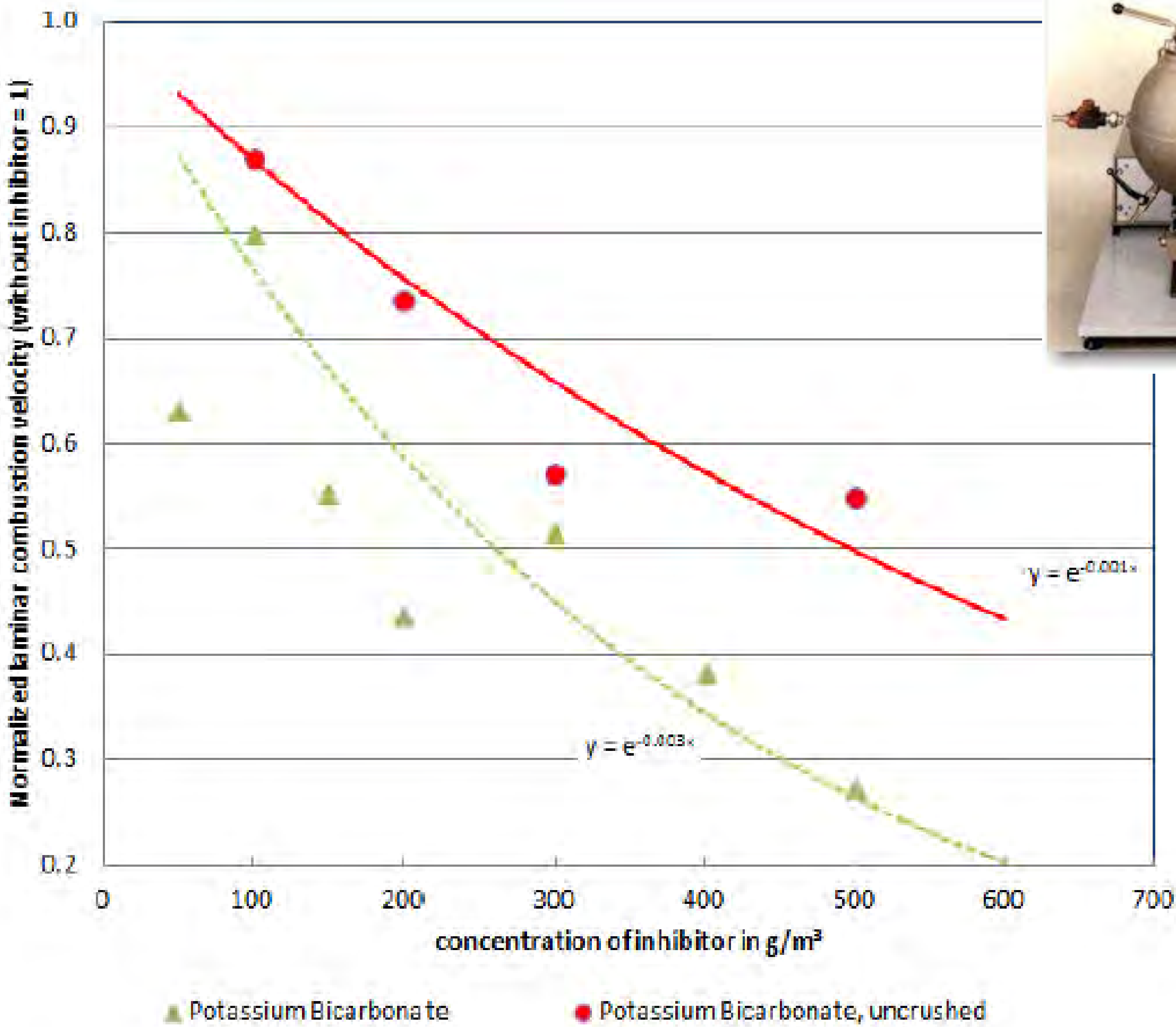
- Laminar combustion velocity (m/s)
- Maximum pressure rise (dP/dt)

103 tests in a 50 m³ module

- Maximum pressure (kPa)
- Flame speed (m/s)

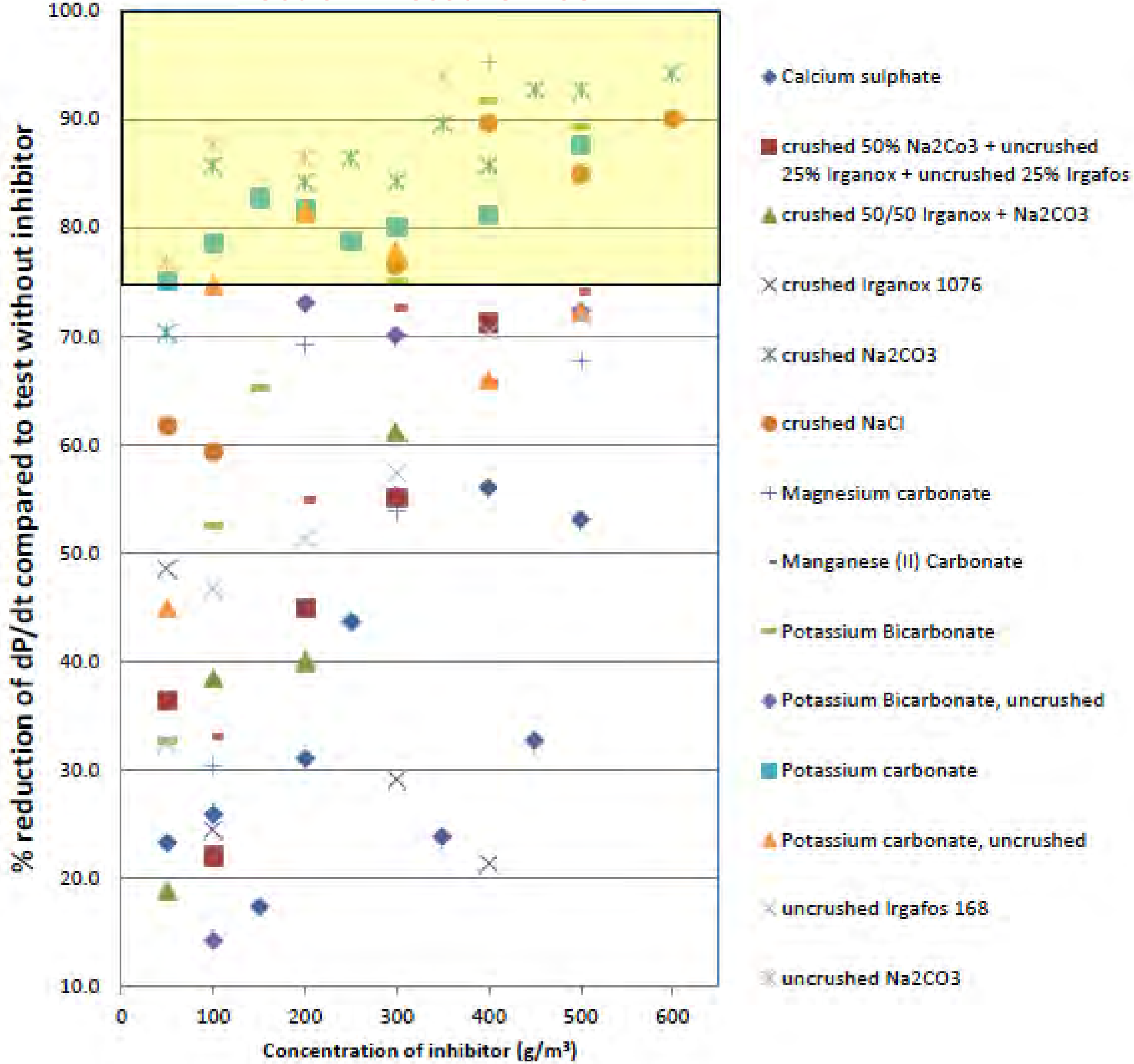
Experimental program 2008-2010



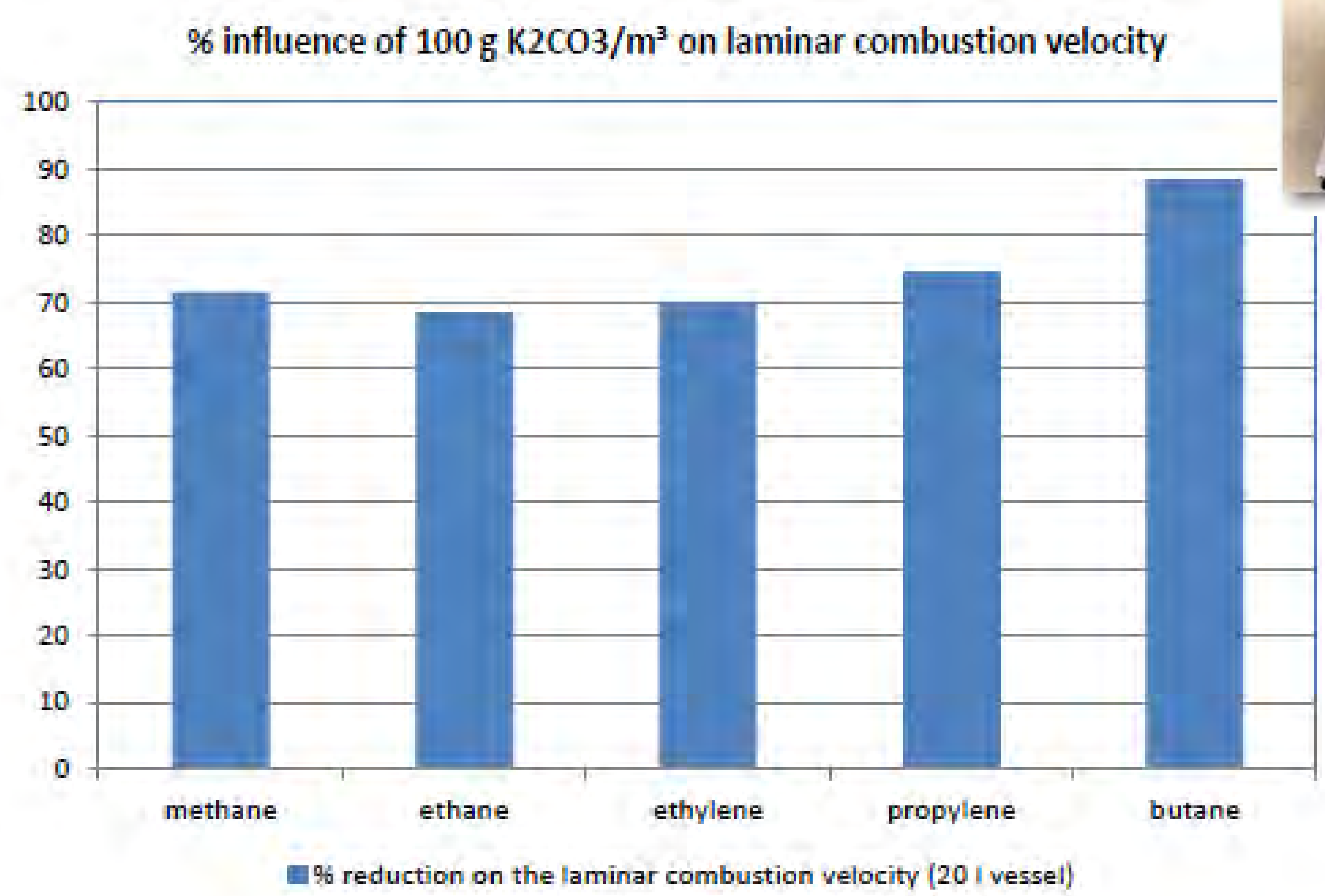


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
Normalized laminar combustion velocity (without inhibitor = 1)
0
100
200
300
400
500
600
700
concentration of inhibitor in g/m³
y = e^-0.001x
y = e^-0.003x
Potassium Bicarbonate
Potassium Bicarbonate, uncrushed

Effect on Pressure Rise



Experimental program 2008-2010



Experimental program 2008-2010

Experimental program 2008-2010

No inhibitor

post - ignition injection of inhibitor

pre-ignition injection of inhibitor

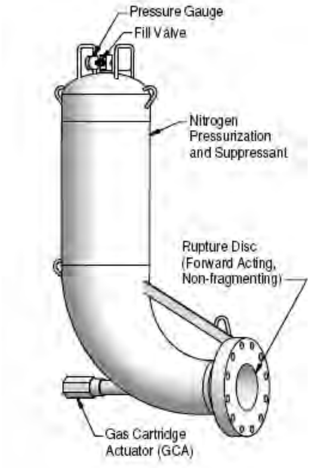
Results in 50 m^3 module

100 g/m³ K_2CO_3

Gas	Average pressure reduction (%)
Methane (9.5%)	96.9
Ethane (5.7%)	94.3
Ethylene (6.6%)	63.7
Propylene (4.5%)	80.2
Butane (3.1%)	97.5

Inhibitor Injection System

Selection of injection technology



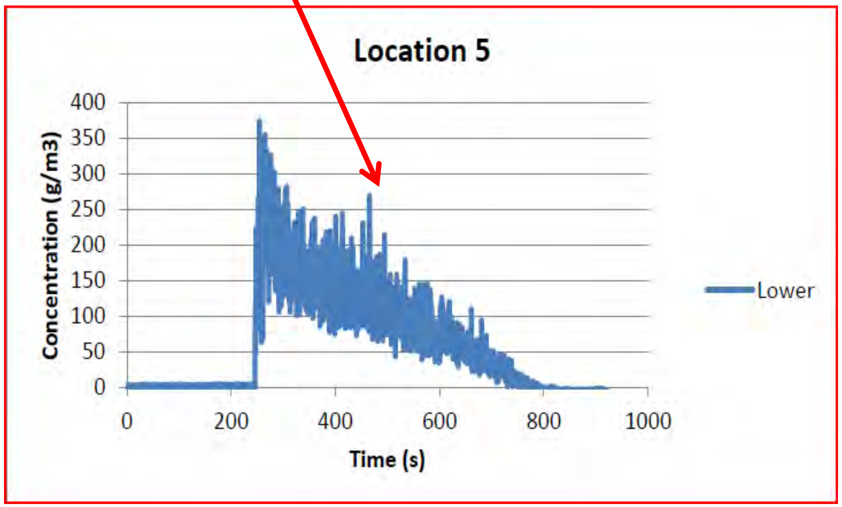
Selection of injection technology

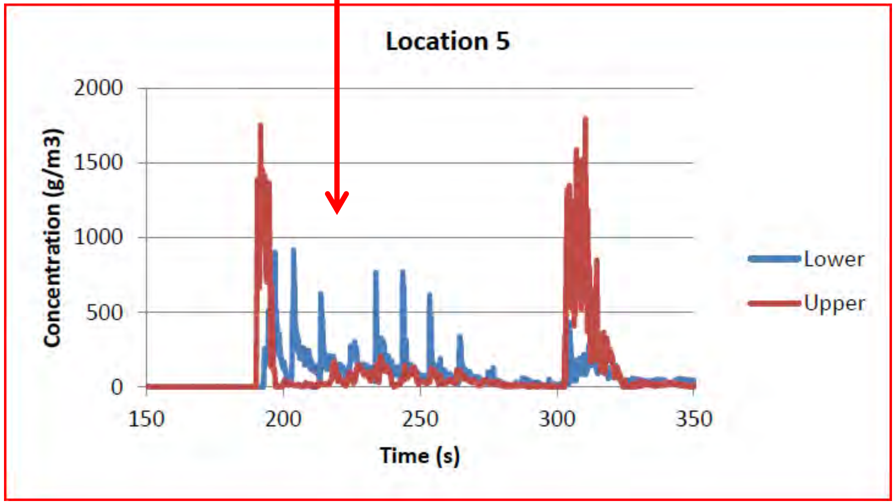
Technology	Possible use for congested areas	Throw length	Size of skid	Multi shot	Volume covered	Quickness of actuation	Interest
Explosion suppression	√	6 m	0.7 m²		400 m3 ?	+++	√
Dry powder fixed pipe	√	15 m	10 m²		As required	+	√
Dry powder monitor		40 m	10 m²		?	+	
Powder fire extinguishing modules	√	?	1 m²	√	150 m3	++	√
Impulse storm		150 m	30 m²	√	10 000 m3	+++	

Selection of injection technology

Continuous injection

Pulsating injection

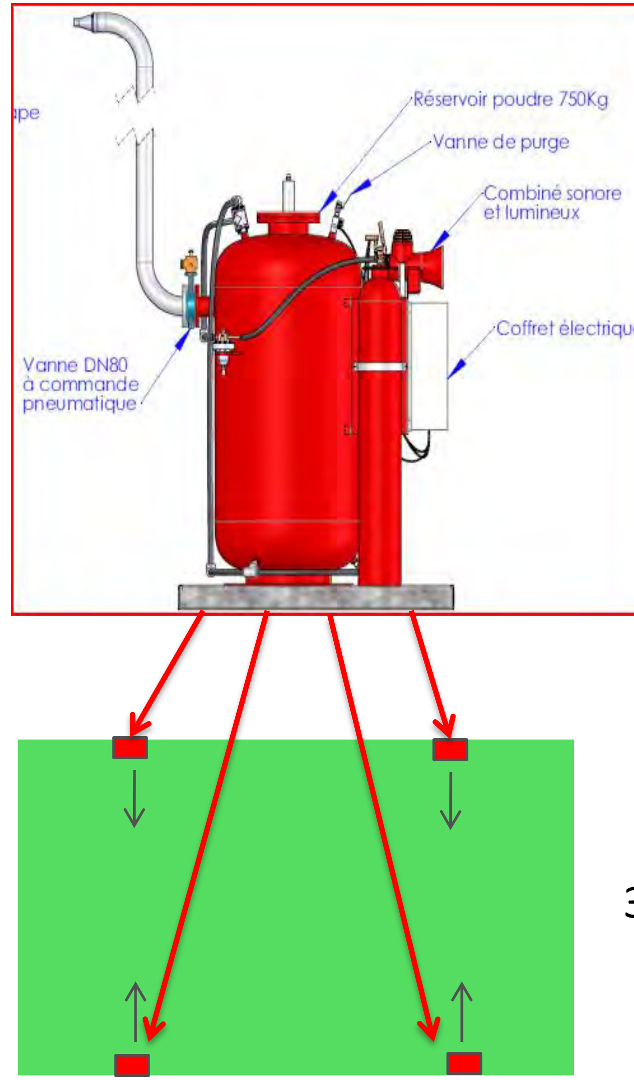




- Settlement of particles is rapid
- A continuous release is the best solution to sustain a homogeneous cloud of inhibitor
- Time between the start of the powder injection and a steady cloud is around 25s

Dispersion testing

Injection system design



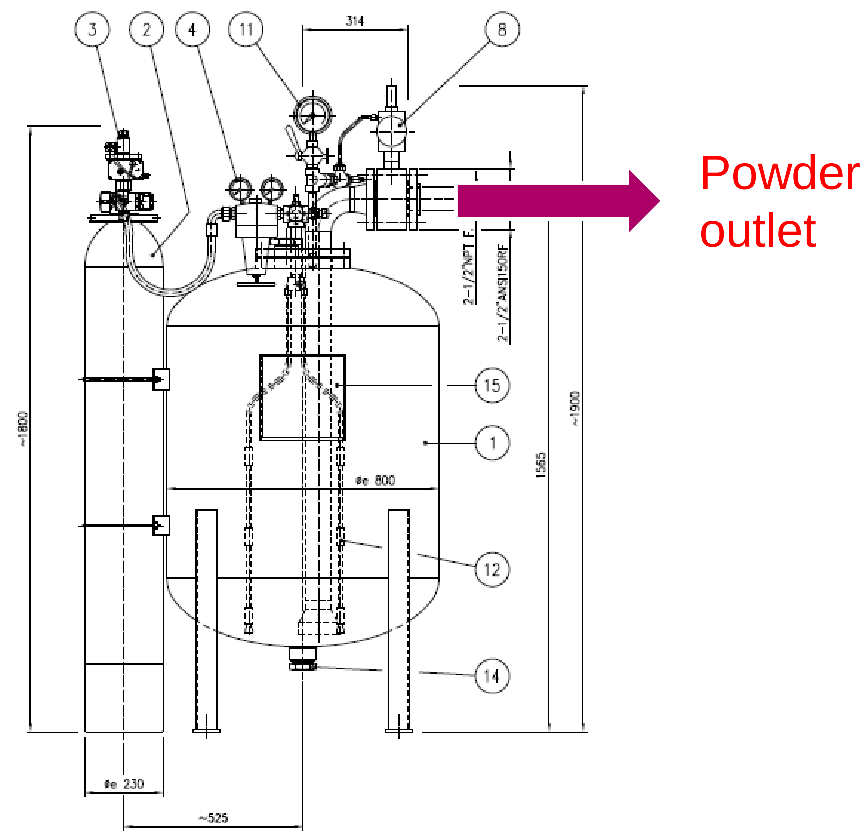
4 meters high

30 m

40 m

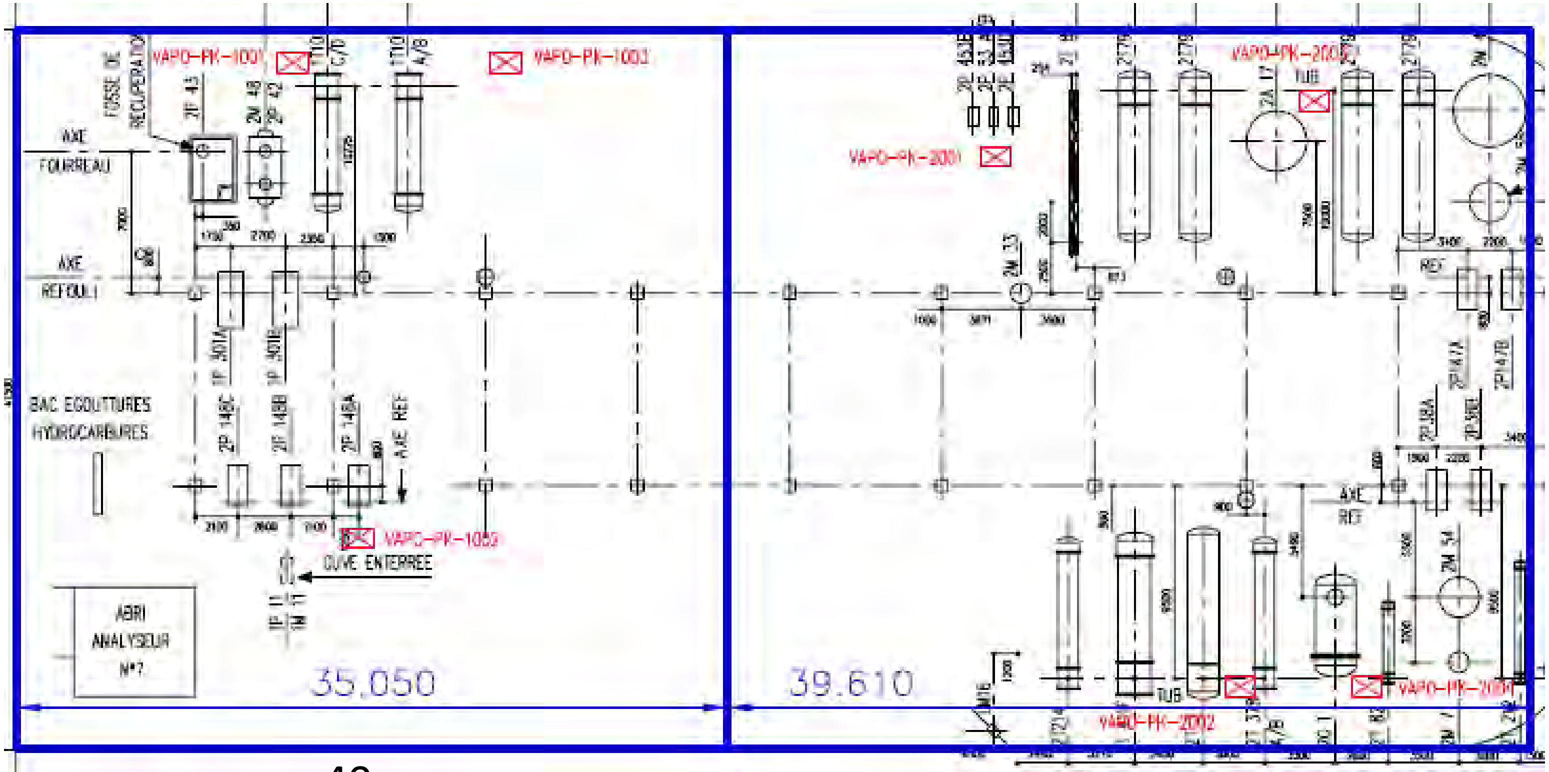
Injection system design

- Skid includes: a storage of powder (500-1000 kg) + 2 bottle of N2 (1 spare) + piping + 1 nozzle
- Inhibitor: commercial dry chemical powder (Bi-Ex 94% sodium bicarbonate), D_{50} = 40 µm
- Volume protected per skid : ~ 1250 m^3
- Storage pressure: 16 barg
- Nitrogen volume : 15 Nm^3 @ 300 barg
- Surface plot: ~1 m^2
- Continuous injection of inhibitor (2 kg/s)
- Pre-ignition strategy
- Dispersion of the cloud of inhibitor : < 1 minute after the start of the leak
- Concentration of the inhibitor in the volume to be protected: 100 g/m^3
- To sustain an efficient cloud of inhibitor during at least 5 minutes



Injection system design

30 m

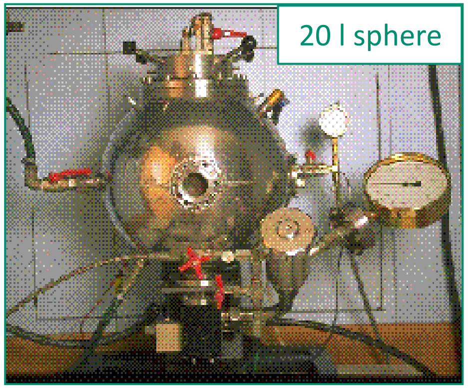


40 m

Future Testing

Large scale experiments

20 l sphere



Explosion testing : OK

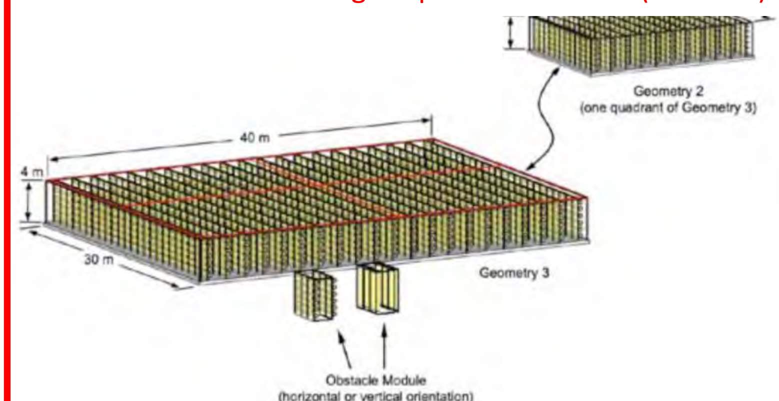
50 m³ module

Explosion testing : OK

Industrial scale (600 m² area)

Dispersion testing : OK

Large experimental scale (2500 m³)



Dispersion & explosion testing

Industrial scale

Application on industrial scale

Industrial Application

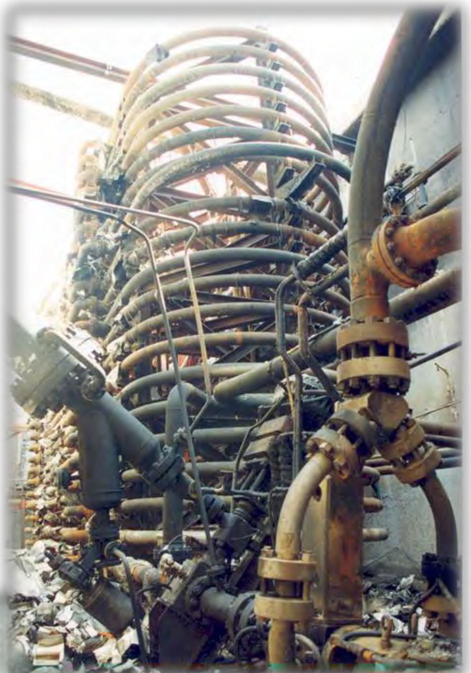
Industrial applications

Industrial applications

Industrial applications

Explosion in LDPE unit (Poland, August 1999)

Industrial applications



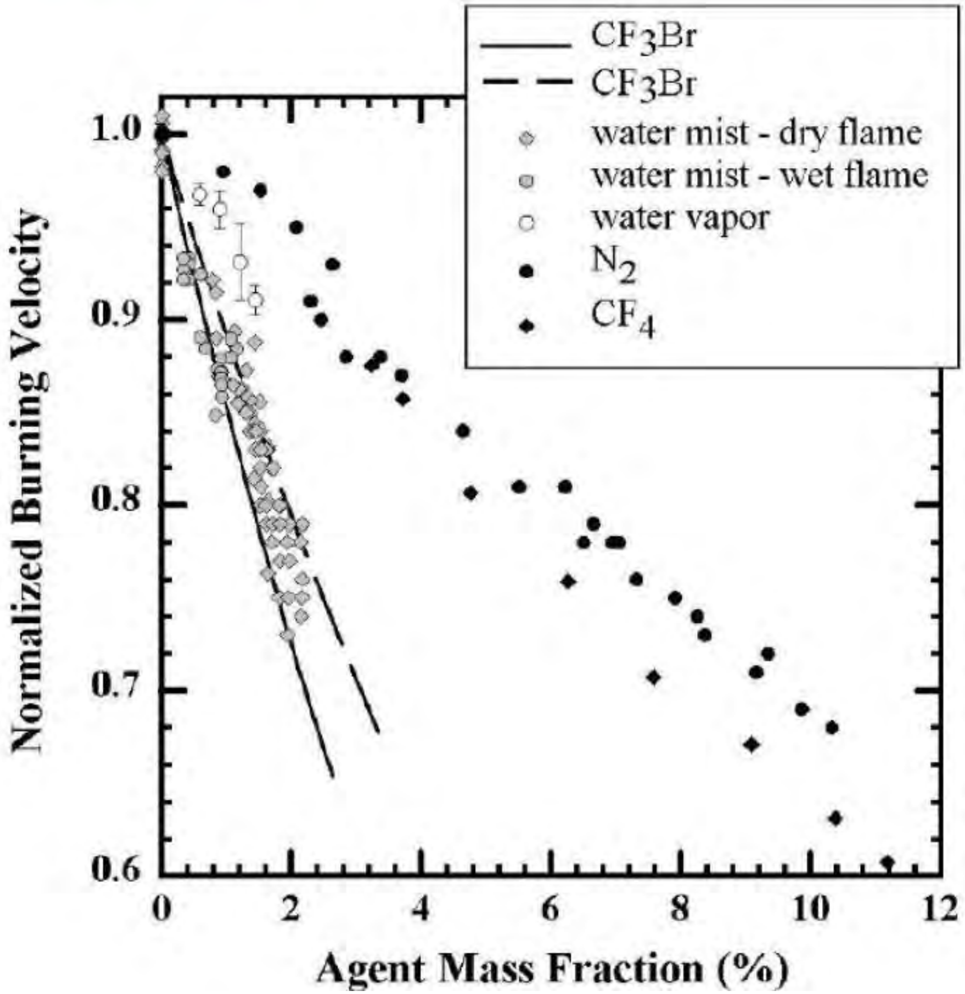
Aqueous Solutions of Inhibitors

Benefits of aqueous solutions of alkali (bi)carbonates

- Combination of flame inhibition by thermal effects of large quantities of water and chemical effects of relatively low quantities of dissolved (bi)carbonates
- Low toxicity of sodium (bi)carbonate and potassium (bi) carbonate solutions
- Availability of sodium (bi)carbonate and potassium (bi) carbonate in large quantities (low price)
- Compatibility with industrial installations (low corrosion rates of (bi)carbonate solutions)
- Possibility of integration with existing firewater systems already installed in existing facilities (to be investigated)
- Easier cleaning of process equipment after discharge

Inhibition by Water Mist

Figure 1 – Normalized burning velocity reduction vs mass of added inhibitor for an inhibited methane-air premixed flame (Fuss et al, 2002)



Effectiveness of Inhibitor Species

Figure 3 – Effectiveness of inhibitor species (Babushok et al, 2000)

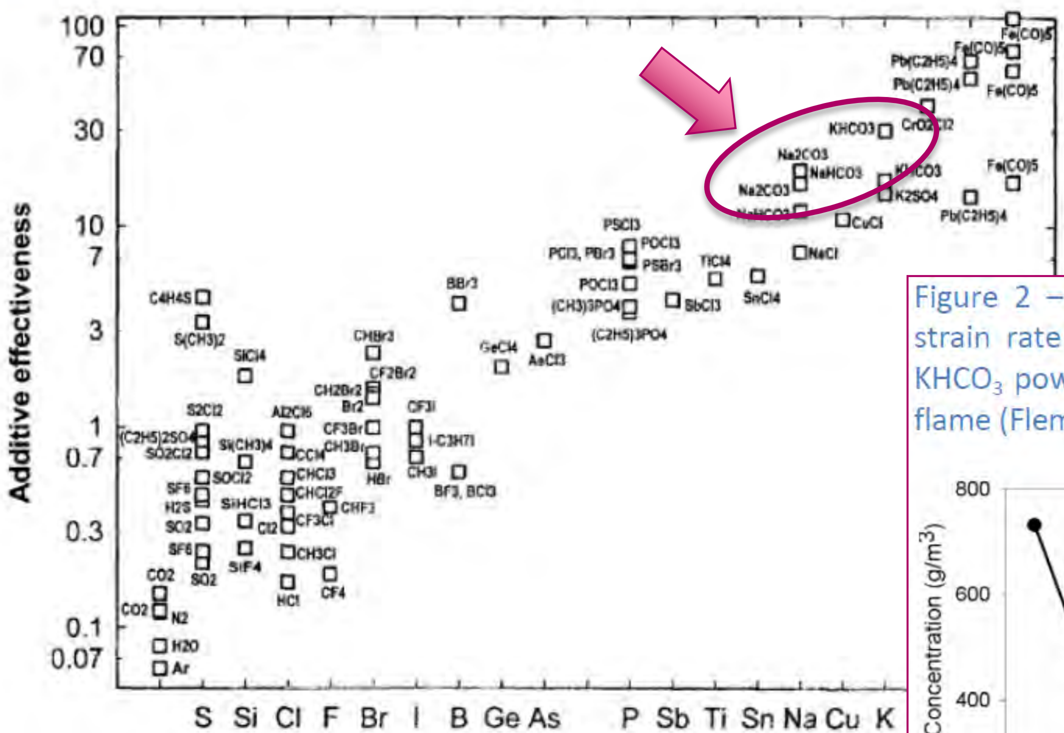
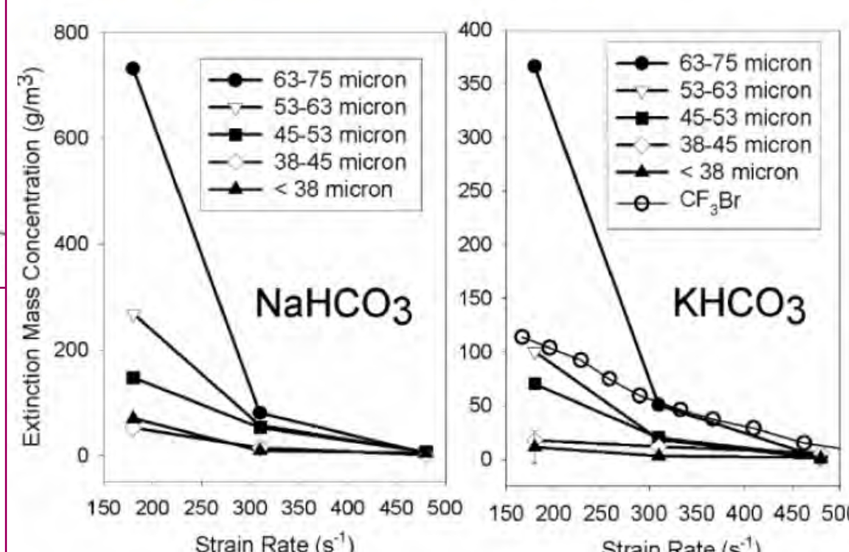


Figure 2 – Extinction mass concentration as a function of strain rate for various particle size ranges of $NaHCO_3$ and $KHCO_3$ powders in a propane/air, counterflow non-premixed flame (Fleming et al, 1998)



Optimum Particle Sizes

- As part of a Phd, a review of literature was conducted to assess the optimum particle size for flame inhibition. The results are summarized in the following table:

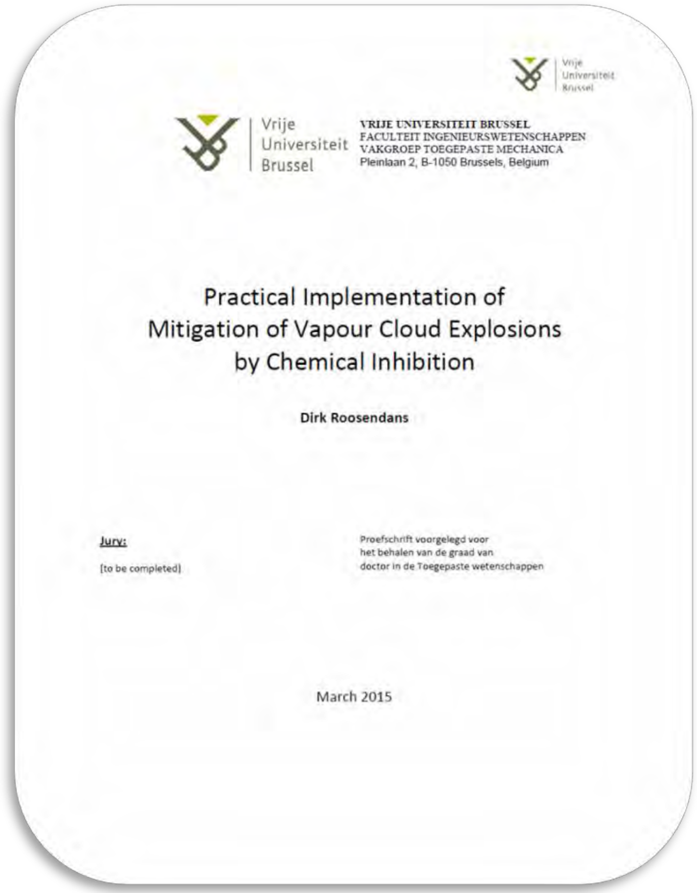
Substance	Flame type	Diameter	Reference
water	Laminar stoechiometric premixed methane/air flame	**10**	Yang et al (2002) Fuss et al (2002) Fleming et al (2002)
water	Laminar non premixed counter flow methane/air flame	**15-20**	Seshadri et al (1978)
water	Laminar non-premixed counterflow propane/air flames	**14**	Chin et al (1983) Fleming et al (2002)
water	Turbulent flames	**10**	Van Wingerden (2000)
water	Turbulent flames	**30**	Acton et al (1990)
water	Turbulent flames	**18**	Sapko et al(1974)
NaHCO3 KHCO3	Laminar propane/air counterflow non-premixed flame	**< 38**	Fleming et al (1998)
NaHCO3	Heptane pan fire	**16**	Ewing et al (1984) Ewing et al (1989)
KHCO3	Heptane pan fire	**22**	Ewing et al (1984) Ewing et al (1989)
NaHCO3	Laminar non-premixed counterflow methane/air-flame	**0-10**	Chelliah et al [2002]
	Turbulent flame	**< 20**	Hoorelbeke [1]
Aqueous NaOH solution	Laminar non-premixed methane/air flame	**10 – 20 µm**	Lazzarini et al. (2000)
Aqueous NaOH solution	Laminar premixed and non-premixed opposed flow flames	**10 – 20 µm**	Wanigarathne et al. (2001) Chelliah et al. (2002)

Optimum Particle Sizes

An optimum particle diameter between **10 – 30 µm** was observed for:

- Laminar flames
- Turbulent flames
- Premixed flames
- Non-premixed flames

This particle size will be the basis for further research on PhD level



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Practical Implementation of
Mitigation of Vapour Cloud Explosions
by Chemical Inhibition

Dirk Roosendans

Jury:
[to be completed]

Proefschrift voorgelegd voor
het behalen van de graad van
doctor in de Toegepaste wetenschappen

March 2015

Experimental setup for additional research

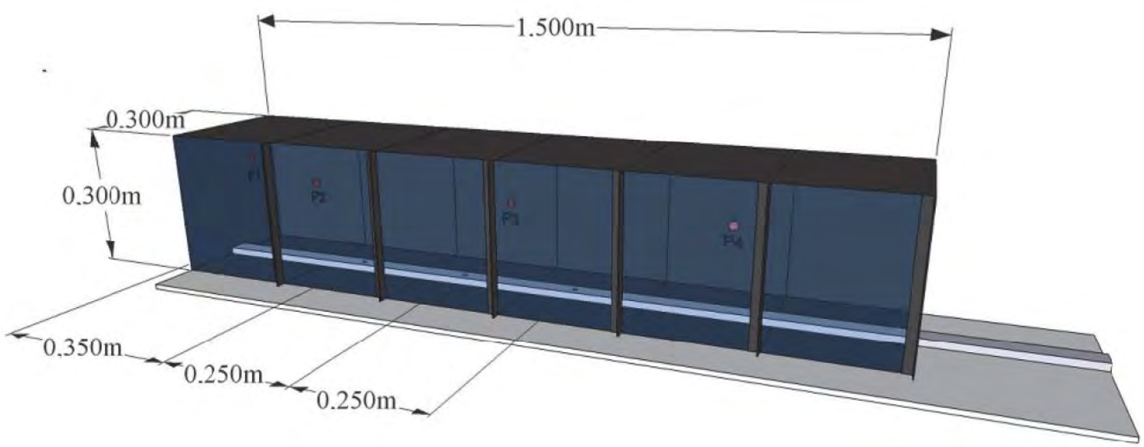
- Small scale test in a channel (0.3 m x 0.3 m x 1.5 m). The aerosol (droplet size < 20 µm) will be created using nozzles in the top of the channel. Experiments will be conducted to investigate the flame behaviour and speed in the channel for different inhibitor concentrations. The selected inhibitors are $KHCO_3$ and $NaHCO_3$.

- Medium scale tests using a 50 m³ module including tests with water deluge with and without inhibitors. These tests include a series of reference experiments with and without the water spray. The experiments with the inhibitor in the water would be performed for the same conditions as for the reference tests

- Possibility to include tests with CF_3Br or other halogenated compounds to investigate use of aqueous solutions of $NaHCO_3$ and $KHCO_3$ as alternative fire suppressants.

Experimental setup for small scale tests

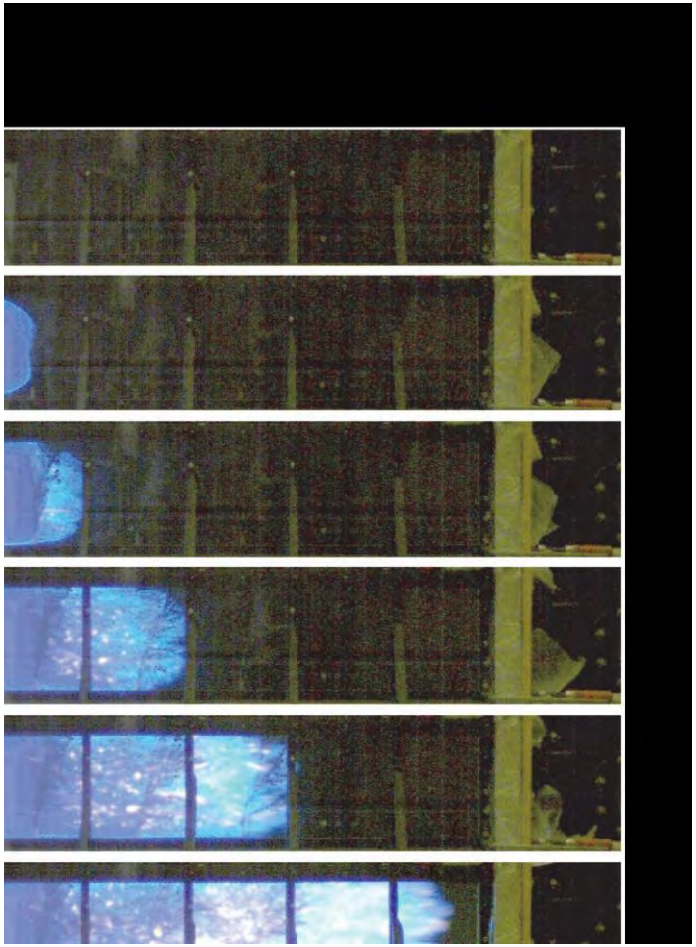
- Mounting of water nozzles in the roof of the channel able to generate droplets with a size < 20 µm
- Pressure measurements and high speed video cameras are used to monitor flame propagation
- Determination of the water droplet size distribution generated by the nozzles (with and without inhibitor)
- Performance of reference tests with and without obstructions (no water or flame inhibitor) using lean, stoichiometric and rich propane-air mixtures.
- Performance of tests using fine water mist varying the water mist concentration (varying spraying time)



Experimental setup for small scale tests

- The tests with the water-inhibitor solutions would be performed for two inhibitors: sodium bicarbonate and potassium carbonate. The amount of inhibitor in the water would be varied. Further, the same variations would be performed as for the pure water mists.

- The results of the experiments would be analyzed in detail concentrating on the effect the different flame inhibiting agents have on the combustion rates in the uncongested and congested channel.



One of the sides of the channel is transparent to allow high speed video filming

Construction of Kinetic Model for K_2CO_3 Inhibition

- Today, there is no developed detailed kinetic models of flame inhibition by potassium compounds available in literature, and fundamental understanding of the mechanism of inhibition by potassium.
- On the other hand several recent studies and estimates demonstrate the interest to the application of potassium-containing compositions in fire suppression systems.
- The lack of kinetic model and clear understanding of inhibition mechanism is a major obstacle to further improvements of the effective use of potassium agents in fire suppression applications.
- The work will be performed in collaboration with NIST (V.I. Babushok, Dr. G.T. Linteris)

NIST
National Institute of Standards and Technology

Questions ?